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Towards a more comprehensive understanding of lacustrine greenhouse gas dynamics — two-year measurements of concentrations and fluxes of CO₂, CH₄ and N₂O in a typical boreal lake surrounded by managed forests

Heli Miettinen¹⁾, Jukka Pumpanen²⁾, Jouni J. Heiskanen³⁾,
Hermanni Aaltonen^{2)*}, Ivan Mammarella³⁾, Anne Ojala¹⁾²⁾, Janne Levula²⁾ and
Miitta Rantakari¹⁾

¹⁾ Department of Environmental Sciences, P.O. Box 65, FI-00014 University of Helsinki, Finland

²⁾ Department of Forest Sciences, P.O. Box 65, FI-00014 University of Helsinki, Finland

³⁾ Department of Physics, P.O. Box 48, FI-00014 University of Helsinki, Finland

* present address: Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland

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Lakes emit terrestrially fixed carbon back to the atmosphere as carbon dioxide (CO₂) and methane (CH₄). Redox conditions in the water columns of lakes typically vary seasonally, and therefore lakes may also be sources of nitrous oxide (N₂O). In this study, we measured the weekly water column concentrations of CO₂, CH₄ and N₂O in a boreal lake and calculated the annual emissions of these gases for the years 2011 and 2012. We found that the emissions of all the gases studied were high right after the ice melt, CH₄ most likely originating from the catchment. Bottom anoxia in summer induced maximum concentrations of CH₄ and N₂O near the sediment, but only elevated the emission of N₂O in autumn 2012. Otherwise, the high concentrations near the sediment did not affect the surface concentrations. The unstable water column in summer 2012 increased the CO₂ and N₂O emissions, but prevented anoxia, and thus decreased the CH₄ concentrations. From the perspective of global warming, the CO₂ emissions were by far the most significant and the relevance of the N₂O emissions was negligible.

Introduction

Growing evidence for the importance of freshwater ecosystems in global greenhouse gas (GHG) balances (e.g. Cole *et al.* 2007, Gudasz *et al.* 2010) has resulted in increasing numbers of studies of GHG in lakes. Lakes receive large amounts of terrestrially fixed carbon, either

directly as carbon gases or in the form of particulate (POM) and dissolved organic matter (DOM). It has been estimated that the amount of this lateral carbon flux in the boreal zone — mainly in the form of organic carbon — is equivalent to as much as 50% of the net ecosystem exchange (NEE) of the forest surrounding the lakes (Rasilo 2013), but is substantially

lower in catchments dominated by mineral soils. Algesten *et al.* (2003) estimated that 30%–80% of this allochthonous, terrestrially fixed carbon is emitted through the lake-atmosphere interface back to the atmosphere as carbon dioxide (CO₂) and methane (CH₄).

Despite growing interest, knowledge of the lacustrine contribution to carbon cycling and GHG emissions is still inadequate. So far, research has focused on CO₂ and CH₄ (e.g. Kling *et al.* 1991, Cole *et al.* 1994, Anderson *et al.* 1999, Eugster *et al.* 2003, Huttunen *et al.* 2003, Sobek *et al.* 2003, Kortelainen *et al.* 2006, Vesala *et al.* 2006, Juutinen *et al.* 2009, López Bellido *et al.* 2011, López Bellido *et al.* 2012a), whereas lake or reservoir studies of nitrous oxide (N₂O) are lacking, especially those considering it simultaneously in combination with carbon gases (Richey *et al.* 1988, Miyajima *et al.* 1997, Huttunen *et al.* 2003, Diem *et al.* 2012). In addition, all the studies on lacustrine N₂O to date have dealt with vertical profiles, while few present time series of N₂O (Mengis *et al.* 1997, Senga *et al.* 2002). Although being quantitatively negligible (e.g. Huttunen *et al.* 2003, 2004), due to its 100-year global-warming potential (GWP) of 298 in comparison with 1 and 25 for CO₂ and CH₄, respectively, information on N₂O can be crucial (Knowles *et al.* 1981, Lemon and Lemon 1981, Priscu *et al.* 1996, Mengis *et al.* 1997, Senga *et al.* 2002). N₂O and CO₂ together also provide a natural platform for integrated studies on nitrogen and carbon cycling and thus a route to unravelling the complexities of aquatic biogeochemistry. The bulk of nitrogen in lacustrine ecosystems originates from terrestrial systems in organic form in DOM and thus enters lakes combined with carbon (Campbell *et al.* 2000, Søndergaard and Thomas 2004). The production processes of these gases (CO₂, CH₄, N₂O) are coupled through consumption of oxygen (O₂) and production of CO₂ in the decomposition of DOM, creating at the same time suitable redox conditions for production of CH₄ and N₂O. Furthermore, decomposition of organic matter (OM) produces nitrate (NO₃⁻), used as a substrate in denitrification and thus N₂O production.

Fluxes, as well as timing of emission peaks, become altered in the course of annual and seasonal changes in precipitation and catchment

hydrology (Anderson *et al.* 1999, Finlay *et al.* 2009, Einola *et al.* 2011, Ojala *et al.* 2011, López Bellido *et al.* 2012b, Rasilo *et al.* 2012). Few studies cover more than one calendar year, which prevents generalizations of the effects of annual changes in hydrology on lacustrine GHG emissions. Furthermore, the sampling frequency in most studies was low, i.e., the systems were sampled only during times assumed to be critical for gas dynamics. Short-term precipitation events can significantly affect both the timing of emissions as well as total annual fluxes (Ojala *et al.* 2011, López Bellido *et al.* 2012b), and with low sampling frequency such events will be missed, resulting in underestimation of the annual fluxes. The lack of long-term observations with better sampling frequency also hampers assessment of the role of water column physics in gas fluxes. To understand the drivers behind the lacustrine GHG fluxes, i.e. whether mainly hydrological, physical or biological, and the role of lakes in landscape-scale carbon balances, knowledge is needed about the annual and interannual variation in these fluxes. Without proper knowledge of the intra-system variation in GHG fluxes, it is also fruitless to compare systems, whether the comparison is between lakes under different disturbance regimes (e.g. catchment forests under management regime or in pristine condition) or systems at different latitudes.

In this study, we measured the concentrations of CO₂, CH₄ and N₂O and estimated fluxes in a typical boreal brown-water lake surrounded by coniferous forests and peatland. Weekly sampling was performed during two calendar years (2011 and 2012), starting at the beginning of the first study year and continuing to freeze-over at the end of the second study year, thus covering two complete growing seasons with more frequent sampling than in most studies published to date. Furthermore, the study years differed in the amounts of precipitation as well as growing season temperatures, giving insight into hydrological drivers and weather-driven differences in interannual variation in GHG fluxes. Such a comprehensive approach sheds light on the combined biogeochemistry of aquatic nitrogen and carbon and leads the way to more detailed studies. It also aids in predicting the role and fate of boreal aquatic ecosystems in future climates,

when shifts in spring floods and timing of ice-out are expected, as well as changes in water column stratification due to higher atmospheric temperatures and dissolved organic carbon (DOC) concentrations as a consequence of increased allochthonous carbon loading from peatlands and forest soil.

Methods

Description of the study lake

Kuivajärvi is a lake located in the boreal zone in central Finland (61°50.743'N, 24°17.134'E). The mean long-term (30-year) annual temperature and precipitation in the area are 3.5 °C and 711 mm, respectively (Pirinen *et al.* 2012). The oblong lake has a surface area of 61.3 ha, length of ca. 2.6 km and maximum depth of ~13 m. The size of the catchment area is 940 ha, as estimated from contour maps. The lake is ~600 m southwest of the Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II station) at an elevation of 141 m a.s.l. The SMEAR II station, located in a managed Scots pine forest (*Pinus sylvestris*), is used for continuous measurements of meteorology, material and energy exchange between the terrestrial ecosystem and atmosphere (Hari and Kulmala 2005). The station also belongs to the European research infrastructure Integrated Carbon Observation System (ICOS). The Kuivajärvi measurements (the so-called Lake-SMEAR Station) form a Supporting ICOS Ecosystem Station. The terrain around the lake is mostly flat, but varies in height by up to 40 m. The primary soil type is Haplic Podzol, and a thin layer of soil at most 2 m deep sits above igneous and metamorphic bedrock. In addition to the managed pine

forests, the catchment area also consists of small amounts of peatland and agricultural land. There are four lakes upstream of Kuivajärvi: Pirttijärvi (area 13.8 ha), Mustalammi (area 1.1 ha), Pii-kainlammi (1.3 ha), and Saarijärvi (area 15.3 ha). The lake is humic with a median surface-water DOC concentration of 11.8 mg l⁻¹ in 2011 and 13.8 mg l⁻¹ in 2012 (Table 1). Furthermore, it is mesotrophic; in 2011 and 2012 the median annual surface-water total nitrogen (N_{tot}) concentrations were 370 µg l⁻¹ and 430 µg l⁻¹, respectively, and the total phosphorus (P_{tot}) concentrations were 14 µg l⁻¹ and 16 µg l⁻¹, respectively (Table 1). Information on the inlet stream draining the catchment can be found in Dinsmore *et al.* (2013).

Sampling and measurements

Sampling, initiated in early 2011, was carried out weekly (4 or 5 times per month) during the open-water period. During the ice-cover period in 2011–2012, the samples were taken once every other week and the sampling covered the time when it was possible to reach the measurement point by foot. The last samples were taken in late November 2012, before the freeze-over. The samples were taken at the deepest point of the lake with a Limnos® water sampler (length 30 cm, volume 2.0 dm³). The sampling covered the entire water column, starting from the surface water (0.1 m) and continuing at 1–2-m intervals, so that the deepest sample was taken as close to the bottom as possible without disturbing the sediment. Two replicate water samples were taken into 60-ml plastic syringes that were transported immediately after sampling to the laboratory situated next to the study lake. The samples were processed, using the headspace equilibrium

Table 1. Median water-quality characteristics in the surface water (0.1 m) and near the bottom (12 m) in 2011 and 2012.

	Depth (m)	DOC (mg l ⁻¹)	PO ₄ (µg l ⁻¹)	P _{tot} (mg l ⁻¹)	NO ₃ -N (mg l ⁻¹)	N _{tot} (mg l ⁻¹)	Chlorophyll <i>a</i> (µg l ⁻¹)
2011	0.1	11.8	3.8	0.014	0.010	0.37	4.8*
	12	12.2	5.7	0.021	0.077	0.50	
2012	0.1	13.8	4.1	0.016	0.048	0.43	2.7*
	12	14.1	5.6	0.021	0.099	0.48	

* Taken from the illuminated layer.

technique within 2 h of arriving in the laboratory. In the laboratory, 30 ml of water was pushed out from syringes, 30 ml of N_2 gas was added and then the syringes were placed in a water bath at 20 °C for 30 min. Then the N_2 -filled syringes were equilibrated by shaking vigorously for 3 min. The samples of the syringe headspace gas were stored in airtight pre-evacuated 12 ml Exetainer® vials (Labco Ltd., Lampeter, Ceredigion, UK) by injecting the gas with a needle through a rubber cork and stored at 5 °C. We stored control samples with known gas concentrations at the same time to ensure that there was no leakage of gases during the storage. The CO_2 , CH_4 and N_2O were measured later at the Hyytiälä Forestry Field Station. The samples from the Exetainer® vials were delivered using an autosampler unit (Gilson GX-271 liquid handler; Gilson Inc., Middleton, WI, USA), carrying a total of 220 gas samples, through a Gilson minipuls 3 into an Agilent 7890 A GC system (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph equipped with a flame-ionization detector (300 °C, for CH_4 , CO_2), electron-capture detector (350 °C, for N_2O) and thermal conductivity detector (250 °C, for CO_2) (oven temperature 60 °C and helium as a carrier gas). As a standard, we used 6-point line calibration with endpoints of 367 and 15 000 ppm for CO_2 , 0.4 and 5.0 ppm for CH_4 , and 0.284 and 0.600 ppm for N_2O . The concentrations of CO_2 , CH_4 and N_2O in lake water were calculated, using Henry's Law and the appropriate temperature relationships.

Water temperature (°C) and dissolved O_2 concentration ($mg\ l^{-1}$) were measured with an optical temperature-compensated dissolved oxygen meter (YSI ProODO, Yellow Springs Instruments, Yellow Springs, OH, USA). The measurements were taken at 0.5-m intervals between the surface water (0.1 m) and 9 m and deeper than 9 m at 1-m intervals down to near the sediment. We defined the epilimnion and the hypolimnion for the thermal stratification periods on the basis of the temperature measurements by assuming the metalimnion at the depth with the steep thermal gradient. We measured the amount of chlorophyll *a* (Chl *a*) in the illuminated euphotic layer (between 0.2 m and 2.5–3.5 m), which was determined during each sampling occasion by multiplying the optical depth measured with a

Secchi disk by a factor of 2. Samples for water-quality analyses were taken monthly from the depths of 0.1 m and 12 m. Total phosphorus (P_{tot}), and total and nitrate nitrogen (N_{tot} and NO_3^-N , respectively) were determined in an authorized laboratory (Finnish Forest Research Institute, METLA) with standard methods. Phosphate phosphorus (PO_4-P) was determined spectrophotometrically at the Hyytiälä Forestry Station with a standard method (SFS-EN ISO 6878), using a Shimadzu ultraviolet (UV)-1800 spectrophotometer (Shimadzu Corp., Kyoto, Japan). DOC and Chl *a* were determined as described in Ojala *et al.* (2011), Chl *a* at the Helsinki University Aquatic Sciences Laboratory with a UV-1800 UV-Visible Recording Spectrophotometer (Shimadzu, Kyoto, Japan), and DOC in 2011 at the Hyytiälä Forestry Station with a Shimadzu total organic carbon (TOC) TOC5000A analyser and in 2012 at the Helsinki University Aquatic Sciences Laboratory with a TOC analyser TOC-V_{CPH} and autosampler ASI-V (Shimadzu, Kyoto, Japan).

Information on the bathymetry was obtained from the Finnish Environment Institute (Oiva database, available at <https://wwwp2.ymparisto.fi/scripts/oiva.asp> [in Finnish]). Wind speed was measured at the SMEAR II station at a height of 23 m. This height was chosen, because the forest around the measuring station is approximately 16 m high and the measurements had to be taken above the canopy layer. These measurements were corrected by dividing the wind speed readings by 1.19 to correspond to the situation above the lake. The coefficient 1.19 was calculated, based on the measured wind speeds close to the surface of Kuivajärvi, using the formula from Paulson (1970). The combined information on water temperature, bathymetry and wind speed was used to calculate the Lake Number (LN) describing water column stability and mixing dynamics, which are crucial for gas transport in the water column and lake–atmosphere fluxes (Imberger and Patterson 1990, López Bellido *et al.* 2012b). LN was calculated with the Lake Analyzer 3.4 program (Read *et al.* 2011, <http://www.gleon.org>).

Gas flux calculations

We estimated the lake–atmosphere gas fluxes

from the surface-water gas concentrations, according to Wanninkhof and Knox (1996):

$$F_{\text{gas}} = \alpha k_{\text{gas}} (C_{\text{gas}} - C_{\text{eq}}) \quad (1)$$

where F_{gas} is the lake–atmosphere flux of the gas studied (here CO₂, CH₄ or N₂O), k_{gas} is the transfer velocity (cm h⁻¹) for the given gas, C_{gas} is the concentration of the gas in the surface water (mmol l⁻¹ or μmol l⁻¹) and C_{eq} is the concentration of the gas (mmol l⁻¹ or μmol l⁻¹) in the surface water in equilibrium with the atmosphere. In this humic lake with low pH, we assumed chemical enhancement factor α for k_{gas} to equal 1.

The *in-situ* equilibrium concentrations of CO₂, CH₄ and N₂O in the lake surface water were calculated according to Henry's Law, with appropriate corrections for the *in-situ* temperature, assuming atmospheric concentrations of 386 ppm for CO₂, 1.91 ppm for CH₄ according to the measurements at the nearby SMEAR II station, and 324 parts per billion (ppb) for N₂O (319 ppb in 2005 and a 0.8-ppb increase per year (IPCC 2007)).

The k_{CO_2} and k_{CH_4} values were determined from the chamber measurements of F_{CO_2} and F_{CH_4} performed 14 times in 2011 between August and November together with the simultaneous C_{CO_2} and C_{CH_4} measurements (cf. Cole *et al.* 2010). The averages of these 14 measurements were used as estimates for k_{CO_2} and k_{CH_4} throughout the study period. The velocities were calculated according to Eq. 1, using the chamber measurement for F_{gas} and the surface-water C_{gas} value. The k_{CO_2} values determined by this method are in good agreement with the k value measured with the eddy covariance (EC) technique at the same time (J.J. Heiskanen unpubl. data). We did not have chamber measurement data for N₂O, and therefore we calculated the $k_{\text{N}_2\text{O}}$ value, using the measured values of k_{CH_4} , which we transformed into the $k_{\text{N}_2\text{O}}$ values as follows:

$$k_{\text{gas1}}/k_{\text{gas2}} = (\text{Sc}_{\text{Gas1}}/\text{Sc}_{\text{Gas2}})^{-n} \quad (2)$$

where Sc_{gas} is the Schmidt number for a given gas. The Sc_{CH_4} value was based on studies by Jähne *et al.* (1987) and Wania *et al.* (2010) and the $\text{Sc}_{\text{N}_2\text{O}}$ value on the study by Wanninkhof (1992). Guérin *et al.* (2007) suggested that $n = 2/3$ for wind

speeds < 3.7 m s⁻¹ and $n = 1/2$ for wind speeds > 3.7 m s⁻¹. We used $n = 1/2$, because the long fetch in Kuivajärvi results in reasonably high wind speeds in this oblong lake, in general higher than 3.7 m s⁻¹ (results not shown). The bubbling of CH₄ was not measured, and thus, the total flux estimates of CH₄ are conservative (Bastviken *et al.* 2004). However, the possible bubbles trapped in ice were checked in Kuivajärvi in early winter 2011 and none was found in the pelagic zone of the lake; only a small area in the littoral zone had trapped bubbles (K. Walther Anthony & A. Ojala pers. comm.).

Statistical analysis

The Pearson correlations (r_p) were determined between the gas concentrations (CO₂, CH₄, N₂O) and the water-quality variables (O₂, P_{tot}, N_{tot}, NO₃-N, PO₄-P, DOC, Chl *a*). Furthermore, differences in the gas fluxes between the study years were evaluated using the *t*-test. All the statistical analyses were performed with IBM SPSS Statistics 21 (IBM Corp., Armonk, NY, USA).

Results

Weather conditions in the study years

The mean air temperature in 2011 was 5.5 °C, i.e. over 2 °C higher than in 2012, when it was 3.2 °C. The difference between the study years was similar during the summer months (June–August), when the mean summer temperatures in 2011 and 2012 were 16.6 °C and 14.1 °C, respectively (Fig. 1). The study years also differed in the amounts of precipitation; the mean annual precipitation was 769 mm in 2011 and 917 mm in 2012 (Fig. 1). During June–August, the corresponding amounts were 255 mm and 306 mm, respectively.

CO₂

In both study years, the highest surface water C_{CO_2} values were recorded just after ice-out in early May (Fig. 2). As a consequence, the

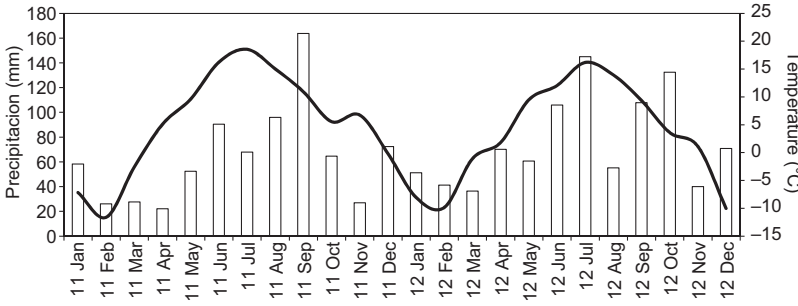


Fig. 1. Monthly mean temperature (°C) (solid line) and precipitation (mm) (bars) in 2011 and 2012.

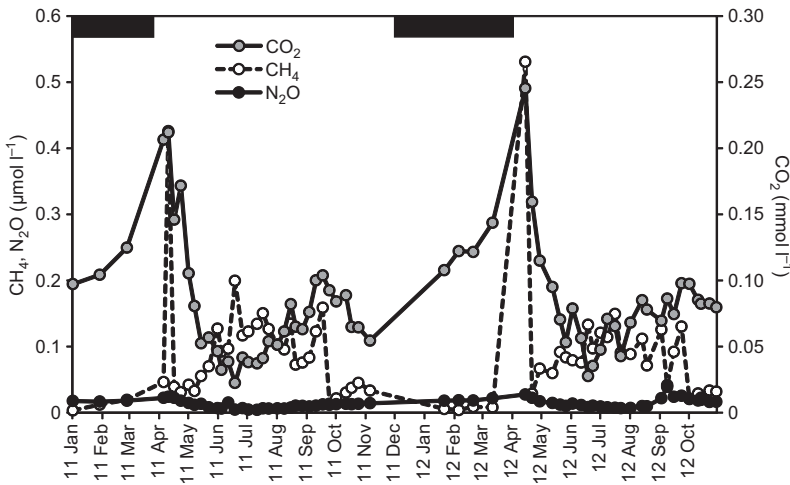


Fig. 2. CO_2 (mmol l^{-1}), CH_4 ($\mu\text{mol l}^{-1}$) and N_2O ($\mu\text{mol l}^{-1}$) concentrations in the surface water (0.1 m) of Kuivajärvi in 2011 and 2012. The horizontal black bars denote the ice-cover period. Note the different scales and axes.

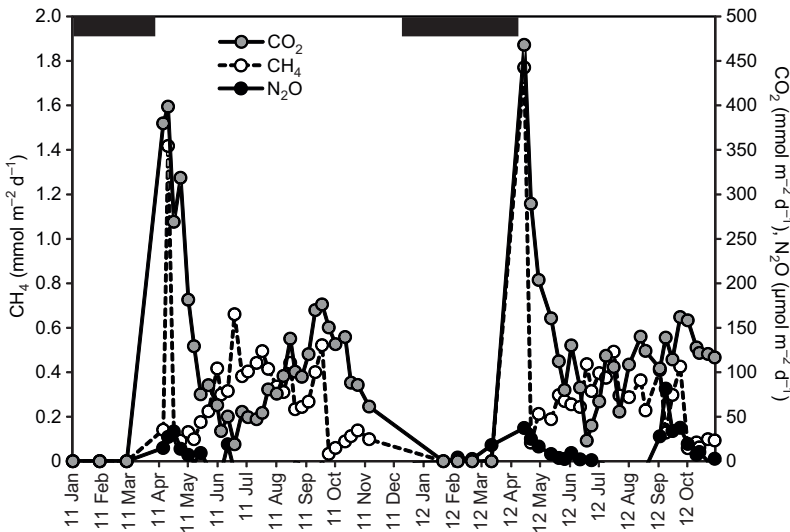


Fig. 3. Daily fluxes of CO_2 ($\text{mmol m}^{-2} \text{d}^{-1}$), CH_4 ($\text{mmol m}^{-2} \text{d}^{-1}$) and N_2O ($\mu\text{mol m}^{-2} \text{d}^{-1}$) from Kuivajärvi in 2011 and 2012. The horizontal black bars denote the ice-cover period. Note the different scales and axes.

peaks in the F_{CO_2} values appeared concomitantly with ice-out (28 April in 2011 and 7 May in 2012) (Fig. 3). The peak C_{CO_2} values were 0.21 mmol l^{-1} and 0.25 mmol l^{-1} in 2011 and 2012, respectively, and the elevated C_{CO_2} values were

measured during most of May in both years (Figs. 2 and 4a). The C_{CO_2} values in the surface water were constantly throughout the year 1.5–10 times above the atmospheric equilibrium level. The minimum annual concentrations at

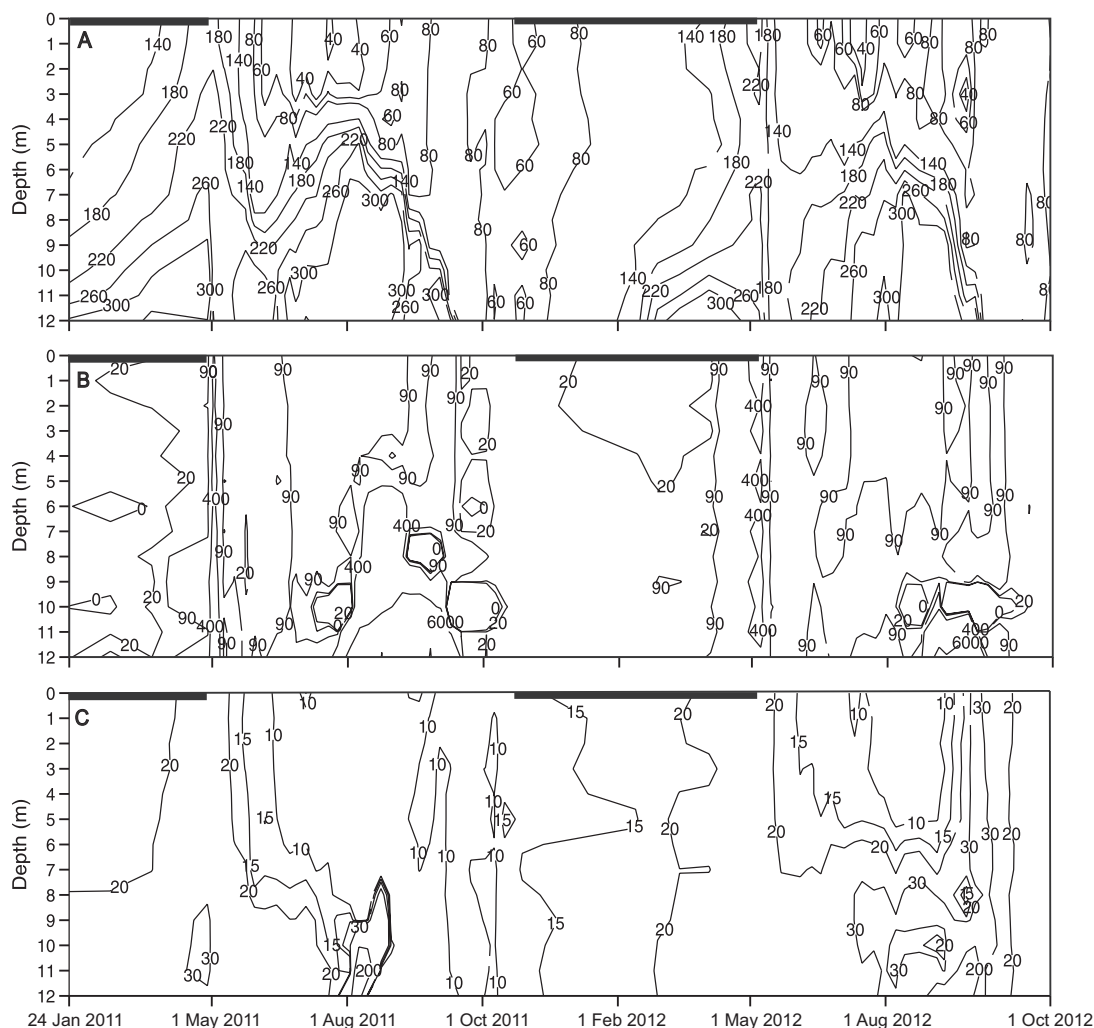


Fig. 4. Water column concentrations of (a) CO_2 ($\mu\text{mol l}^{-1}$), (b) CH_4 (nmol l^{-1}), and (c) N_2O (nmol l^{-1}) during the study period 2011–2012. The horizontal black bars denote the ice-cover period.

the surface were recorded in mid-July, with the values of $0.022 \text{ mmol l}^{-1}$ and $0.035 \text{ mmol l}^{-1}$ for 2011 and 2012, respectively (Fig. 2). Later, the concentrations began to slowly increase and reached the autumn maxima of 0.10 mmol l^{-1} and $0.098 \text{ mmol l}^{-1}$ in mid-October in 2011 and 2012, respectively (Fig. 2). In the epilimnion, the CO_2 showed a weak and negative correlation (Pearson correlation coefficient) with Chl *a* ($r_p = -0.397$, $n = 43$, $p < 0.008$), indicating possible biological control.

The CO_2 concentrations near the bottom increased during winter and peaked before ice-out (0.37 mmol l^{-1} and 0.31 mmol l^{-1} in 2011

and 2012, respectively) (Figs. 4a and 5). After the spring minimum, the CO_2 concentrations close to the sediment began to increase and were also high at the end of the summer stratification in August and early September (0.32 – 0.39 mmol l^{-1}) (Figs. 4a and 5). The elevated CO_2 concentrations lasted longer both in the surface and bottom layers than the CH_4 and N_2O concentrations, which peaked for only short periods (Figs. 2 and 5) as did the fluxes in spring (Fig. 3).

The temperature profiles indicated incomplete spring turnover in 2011 and a complete but very short turnover in spring 2012 (Fig. 6a). The CO_2 profiles also constitute proof of ineffi-

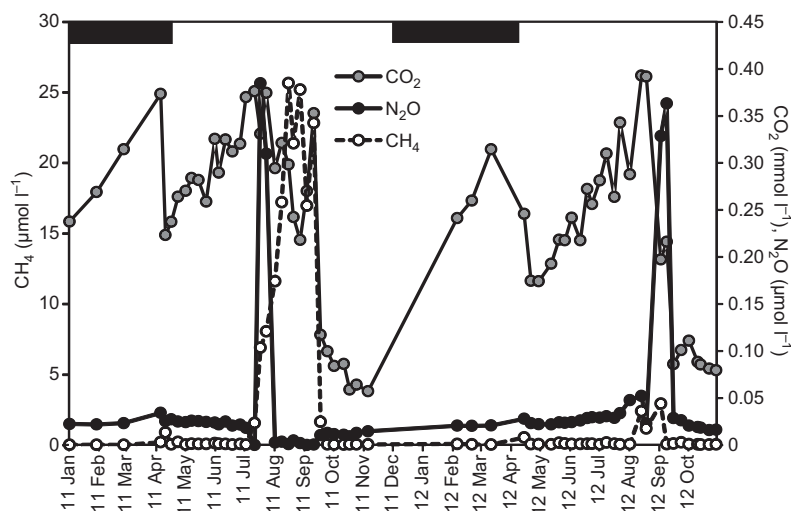


Fig. 5. CO_2 (mmol l^{-1}), CH_4 ($\mu\text{mol l}^{-1}$) and N_2O ($\mu\text{mol l}^{-1}$) concentrations in the hypolimnion (12 m) of Kuivajärvi in 2011 and 2012. The horizontal black bars denote the ice-cover period. Note the different scales and axes.

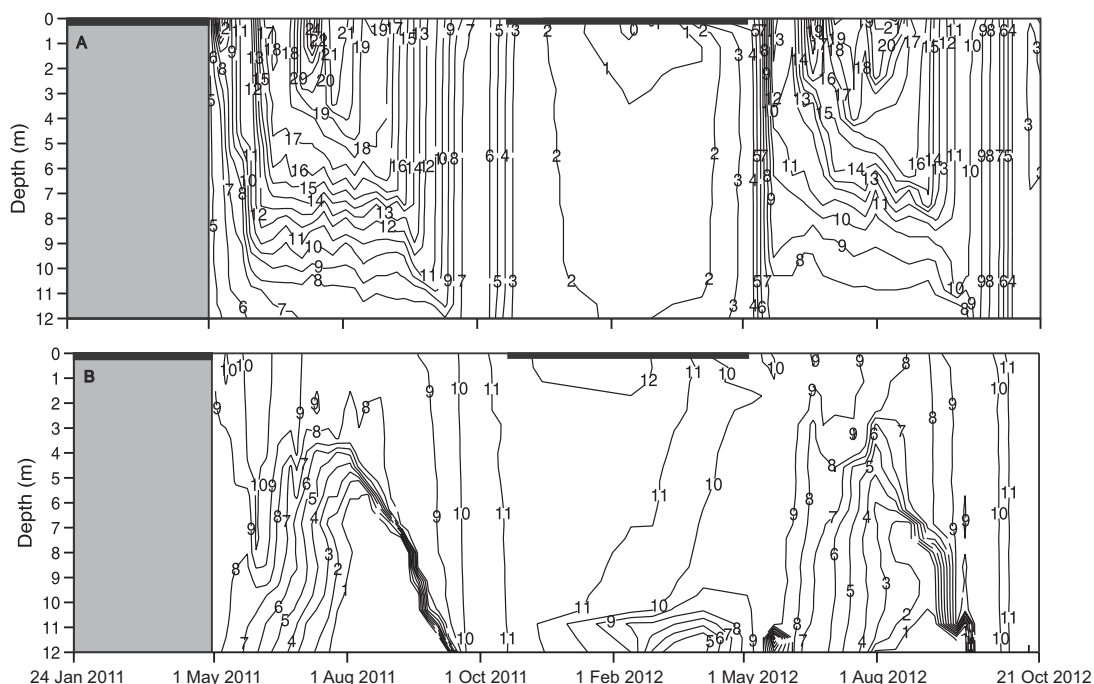


Fig. 6. Water column (a) temperature ($^{\circ}\text{C}$) and (b) oxygen concentrations (mg l^{-1}) during the study period 2011–2012. The vertical grey areas denote periods at the beginning of the observation period with no measurements. The horizontal black bars denote the ice-cover period.

cient spring mixing, especially in 2011 (Fig. 4a). The hypolimnetic CO_2 concentrations increased during the stratification periods simultaneously with decreasing O_2 concentrations (Fig. 6b), indicating that intralake carbon mineralization was the main source of CO_2 in the hypolimnion. Throughout the dataset, the CO_2 concentrations

correlated negatively with the O_2 concentrations ($r_p = -0.85$, $n = 402$, $p < 0.0001$), and the correlation was also negative in the hypolimnion ($r_p = -0.87$, $n = 147$, $p < 0.0001$). In autumn, the water column was completely mixed in both years and the CO_2 concentrations decreased rapidly in hypolimnion (Fig. 4a). However, the F_{CO_2} values

increased only slightly in autumn, probably due to gradual deepening of the thermocline, and thus the excess CO_2 from the deep layers was released over several weeks (Fig. 3).

During the ice-cover period, the CO_2 concentrations throughout the water column slowly increased (Fig. 4a), contributing to the CO_2 emission peaks of $0.40 \text{ mol m}^{-2} \text{ d}^{-1}$ and $0.47 \text{ mol m}^{-2} \text{ d}^{-1}$ immediately after ice-out in 2011 and 2012, respectively (Fig. 3). In both study years, the emissions dropped close to $0.02 \text{ mol m}^{-2} \text{ d}^{-1}$ after the spring peak and began to increase gradually in summer, reaching the maximum in mid-October, i.e. 0.17 and $0.16 \text{ mol m}^{-2} \text{ d}^{-1}$ in 2011 and 2012, respectively. However, in 2011 the increase in F_{CO_2} values was fairly smooth, whereas in 2012 several small emission peaks occurred during summer (Fig. 3). The total annual CO_2 emission from Kuivajärvi was 24 mol m^{-2} and 27 mol m^{-2} in 2011 and 2012, respectively. The total emission in May 2011 was 7.4 mol m^{-2} over 30 d, which was 31% of the total annual emission. In May 2012, the total springtime emission was 6.6 mol m^{-2} , which was 24% of the total emission. The summertime (June–August) CO_2 emission in 2011 was 5.7 mol m^{-2} , contributing 24% to the total emission. The corresponding summertime figures for 2012 were 9.6 mol m^{-2} and 35%, respectively. Most of the emissions occurred in autumn; in September–October they were 10.7 and 11.2 mol m^{-2} and formed 45% and 41% of the total annual emissions in 2011 and 2012, respectively.

CH_4

During the open-water period, the surface water C_{CH_4} values were constantly ~ 30 times above the atmospheric equilibrium level and the CH_4 concentrations in the epilimnion correlated negatively with the O_2 concentrations ($r_p = -0.774$, $n = 152$, $p < 0.0001$). The C_{CH_4} values peaked briefly after ice-out, reaching the values of $0.43 \mu\text{mol l}^{-1}$ and $0.53 \mu\text{mol l}^{-1}$ in 2011 and 2012, respectively (Fig. 2). Later, the surface water C_{CH_4} values slightly increased from June onwards and remained above $0.1 \mu\text{mol l}^{-1}$ for most of the summers in both study years (Fig. 2). A similar pattern was found in the F_{CH_4} values, i.e. after the

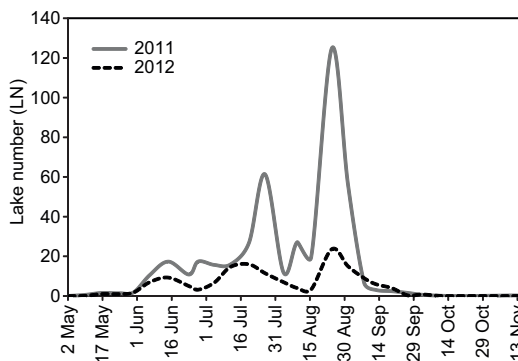


Fig. 7. Lake Number in Kuivajärvi from early May to mid-November in 2011 and 2012.

very sharp flux peaks of $1.41 \text{ mmol m}^{-2} \text{ d}^{-1}$ (2011) and $1.80 \text{ mmol m}^{-2} \text{ d}^{-1}$ (2012) in spring, the CH_4 emission collapsed but gradually increased during summer, reaching the summer maximum in July, approximately $0.50 \text{ mmol m}^{-2} \text{ d}^{-1}$ in both study years (Fig. 3). In mid-July 2011, there was a sudden peak in the C_{CH_4} concentration and emission ($0.20 \mu\text{mol l}^{-1}$ and $0.66 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively) (Figs. 2 and 3). Deeper in the water column, the CH_4 concentrations remained low and the water column was stable; thus the source of CH_4 did not appear to be in the hypolimnion or sediment (Fig. 4b). These peaks were most likely attributable to the heavy rain event on 10 July and the following transport of CH_4 from the catchment or littoral area.

The very high CH_4 concentrations in autumn 2011 in the hypolimnion, up to $25 \mu\text{mol l}^{-1}$ (Figs. 4b and 5), were attributable to the incomplete spring turnover and strong stratification during summer, as clearly shown both in the temperature profiles and LN (Figs. 6a and 7). The strong stratification initiated a rapid decline in O_2 concentration in June 2011 (Fig. 6b). The hypolimnion below 6 m was slightly warmer in 2011 ($< 15^\circ\text{C}$) than in 2012 ($< 13^\circ\text{C}$) (Fig. 6a), thus explaining the rapid consumption of O_2 (Fig. 6b). Despite the concomitant O_2 decline and CH_4 build-up in the hypolimnion, there was no correlation between the CH_4 and O_2 concentrations, due to wide variation in the CH_4 concentrations at the depths of 11 m and 12 m. However, these high hypolimnetic summer concentrations did not result in high F_{CH_4} values in autumn 2011 (Fig. 3). In summer 2012, the

lake water column was less stable until mid-July (Figs. 6a and 7), and the period of hypoxia, and eventually anoxia, was shorter (Fig. 6b), leading to lower CH_4 concentrations in the hypolimnion (Fig. 5). Despite the very different summertime hypolimnetic O_2 conditions and CH_4 concentrations, the CH_4 emissions in autumn were similar in both years (Fig. 3). The hypolimnion remained oxic above 12 m during the winters studied, and there was no significant build-up of CH_4 in winter (Figs. 4b, 5 and 6b). The annual CH_4 emissions in 2011 and 2012 were of similar magnitude: $0.061 \text{ mol m}^{-2} \text{ y}^{-1}$ and $0.056 \text{ mol m}^{-2} \text{ y}^{-1}$, respectively.

Spring and autumn contributed less to the total F_{CH_4} than to the total F_{CO_2} values and half of the emissions occurred in summer. The total spring F_{CH_4} value in May 2011 was $0.0078 \text{ mol m}^{-2}$ over 30 days, which was 13% of the total emission in 2011. In May 2012, the total springtime emission was 0.010 mol m^{-2} , corresponding to 18% of the total emission. The total summertime (June–August) CH_4 emission in 2011 was 0.034 mol m^{-2} , forming 56% of the total emission. The corresponding figures for 2012 were 0.029 mol m^{-2} and 51%, respectively. In autumn (September–October), the emissions were 0.019 and 0.017 mol m^{-2} in 2011 and 2012, respectively, contributing 31% to the total annual emissions in both study years.

N_2O

N_2O was present in the surface water throughout the measuring period, but the $C_{\text{N}_2\text{O}}$ values were low, remaining close to the atmospheric equilibrium (Fig. 2). Therefore in 2011, Kuivajärvi appeared as a small sink of N_2O and in 2012 a small source of N_2O : $-0.47 \text{ mmol m}^{-2} \text{ y}^{-1}$ and $2.4 \text{ mmol m}^{-2} \text{ y}^{-1}$, respectively. The difference in the total annual emissions between the study years was significant (t -test: $t_{29} = 3.203$, $p = 0.0041$). In both years, the N_2O concentrations in the hypolimnion peaked shortly before the O_2 was depleted at the end of the summer stratification (Fig. 5). The maximum concentrations were similar in the study years: $0.38 \mu\text{mol l}^{-1}$ and $0.36 \mu\text{mol l}^{-1}$ in 2011 and 2012, respectively. In 2011, the N_2O concentration peaked in the hypolimnion before the maximum concentra-

tions of CH_4 (Fig. 5). In 2012, the N_2O peak was very similar to that in 2011, but the CH_4 concentrations remained low because the O_2 level near the bottom was $< 1 \text{ mg l}^{-1}$ for only 3 weeks, whereas in 2011 anoxia lasted for more than 2 months (Figs. 5 and 6b). Apart from these short events, the hypolimnetic N_2O concentrations also remained low, and for most of the study years N_2O was rather evenly distributed throughout the water column (Fig. 4c). During winter, the concentrations slowly increased (Fig. 4c), resulting — similar to CO_2 — in an $F_{\text{N}_2\text{O}}$ peak after ice-out: 27 and $37 \mu\text{mol m}^{-2} \text{ d}^{-1}$ in 2011 and 2012, respectively (Fig. 3). The largest $F_{\text{N}_2\text{O}}$ peak was recorded in autumn 2012: $82 \mu\text{mol m}^{-2} \text{ d}^{-1}$ (Fig. 3), appearing simultaneously with the maximum concentration in the hypolimnion, $0.36 \mu\text{mol l}^{-1}$ (Fig. 5) and elevated concentrations throughout the water column (Fig. 4c). The N_2O concentrations correlated with those of NO_3^- ($r = 0.782$, $n = 15$, $p < 0.001$) in the surface water and also near the bottom of the lake (12 m) ($r = 0.644$, $n = 14$, $p < 0.013$), indicating that the main process behind N_2O production, namely denitrification, is NO_3^- -limited in Kuivajärvi.

Discussion

The concentrations of CO_2 and CH_4 in Kuivajärvi were in good agreement with previous measurements taken in 177 randomly selected lakes in Finland (Kortelainen *et al.* 2006, Juutinen *et al.* 2009), but the annual emissions were higher, due to the higher k values in Kuivajärvi. These k values were calculated from direct measurements and thus reliable, whereas in the previous studies the gas transfer coefficients were modelled, based on wind speed. Kuivajärvi was a source of CO_2 throughout the open-water period in both study years, although the emission was clearly lowest in midsummer (July). Another intensively studied lake in Finland, Valkea-Kotinen, located approx. 150 km east of Kuivajärvi, was a small sink of CO_2 in July, although on an annual basis this pristine lake surrounded by old-growth forest was also a net source of CO_2 (Vesala *et al.* 2006). The difference between these two lakes in July can be attributed to the mixing efficiency of the sur-

face water; Valkea-Kotinen is a wind-sheltered lake, providing stable conditions for vigorous growth of flagellated phytoplankton, whereas in the oblong-shaped, wind-exposed Kuivajärvi, the mixing depth typically reaches 2–3 m below the illuminated layer (~0–3 m), thus impeding the life of photosynthetic planktonic organisms (Peltomaa and Ojala 2010). However, a negative correlation between CO₂ and Chl *a* suggests that photosynthesis also regulates the CO₂ concentration in the epilimnion during summer in Kuivajärvi, whereas a clearly negative correlation between CO₂ and O₂ in the hypolimnion suggests *in-situ* decomposition during stagnation. Temperature stratification and water column stability in Kuivajärvi were stronger during the dry and sunny summer in 2011 than in the cold and rainy summer of 2012, while in June–August 2011 the CO₂ emission was lower than in 2012 (*t*-test: $t_{12} = 2.654$, $p = 0.026$), most likely due to increased phytoplankton production decreasing the C_{CO2} values and strong stratification preventing the transport of supplemental CO₂ from the CO₂-rich hypolimnion. This is in agreement with previous studies showing that CO₂ emissions from lakes can exhibit significant interannual variation, although the presence of the biological drivers of fluxes from humic lakes is not often reported (Anderson *et al.* 1999, Rantakari and Kortelainen 2005, Finlay *et al.* 2009).

Although the stratification patterns differed somewhat between the study years, the differences in total fluxes of GHGs were small. The total annual emission of CO₂ appeared slightly higher in 2012, but the difference was not statistically significant (*t*-test). Constant annual effluxes over several years were also observed in the continuous EC measurements in Valkea-Kotinen (Huotari *et al.* 2011). These results suggest that when conditions for demineralization (e.g. temperature in the water column) remain similar between years, the annual differences in stratification rather change the timing of F_{CO_2} , not the total amount of annual emissions. However, higher CO₂ emissions in rainy years than in dry years was reported by Einola *et al.* (2011) and Huotari *et al.* (2009). Rantakari and Kortelainen (2005) found that a rainy summer and autumn contributed to augmented springtime F_{CO_2} values during the following year, probably

as a result of high export of OM from the catchment, suggesting that in Kuivajärvi the high precipitation in summer and autumn 2012 may also have increased the CO₂ concentrations in 2013.

In Kuivajärvi, the CO₂ emissions just after ice-out were up to 31% of the total annual emission in 2011 and over 20% in 2012. This timing of CO₂ emissions differs from that in previous reports from lakes in Finland. In the small forest lake, Valkea-Kotinen, most of the CO₂ was released in autumn and the annual importance of ice-out emission was very small (Huotari *et al.* 2011). Similarly, in the larger and humic lake, Pääjärvi, the F_{CO_2} value after ice-out was very sudden and the high peak lasted only 1 week (Ojala *et al.* 2011), whereas in Kuivajärvi the springtime emission of CO₂ showed a duration of several weeks. In Minnesota, a small woodland lake showed similarly important CO₂ emissions after ice-out (Anderson *et al.* 1999), but the daily springtime emissions were only about half of those measured in Kuivajärvi. Thus, the springtime emissions of CO₂ from Kuivajärvi were high and long-lasting. In the inlet stream of Kuivajärvi, Dinsmore *et al.* (2013) found the highest concentrations of CO₂ in spring at the time of snowmelt and, therefore, part of the excess springtime CO₂ in Kuivajärvi likely originated from the catchment. The incomplete spring turnover in 2011 and a complete but very short turnover in spring 2012 indicated by the temperature profiles also constitute proof of the external source of CO₂ in the surface water.

Although the hypolimnetic CH₄ concentrations were almost 10-fold higher in summer 2011 with prolonged hypoxia/anoxia than in 2012, the annual CH₄ emissions were very similar in both years. In 2011, the sudden disappearance of CH₄ from the hypolimnion at the end of summer stratification could have been due to efficient water column mixing in late September and resulting quick atmospheric release of CH₄. Distinctive, but rapid, CH₄ emissions after ice melt both in 2011 and 2012 suggest that even by weekly sampling, we may have missed the CH₄ emission peak at the end of summer stratification in 2011. In the well-oxygenated Pääjärvi, the daily variation in F_{CH_4} value in autumn was high despite the very low water column concentrations of CH₄ (López Bellido *et al.* 2009). We did not measure

the bubbling of CH_4 , and thus, the values of CH_4 emissions are conservative (e.g. Bastviken *et al.* 2004, Wik *et al.* 2013). Furthermore, we had only one sampling point, and thus we could not demonstrate, whether through lateral transport or action of internal waves, gas-rich water masses were moved, e.g. towards the outlet of the lake. The other possible explanation for the sudden depletion of CH_4 could be efficient methanotrophic activity in the water column. Kankaala *et al.* (2006) showed that in a boreal humic lake, as much as $18 \text{ mmol CH}_4 \text{ m}^{-3} \text{ d}^{-1}$ was consumed by methanotrophs. The maximum CH_4 storage measured in the hypolimnion of Kuivajärvi in summer 2011 was 77 mmol m^{-3} , making methanotrophy a plausible explanation.

López Bellido *et al.* (2012b) reported increased CH_4 concentrations in the water column of a boreal lake after an extreme rain event. Since the elevated concentrations appeared only in the middle of the stratified water column, not in the hypolimnion, they concluded that the CH_4 must have originated in the catchment or littoral area. Our data suggest that a similar phenomenon occurred in mid-July 2011 in Kuivajärvi when the C_{CH_4} values were several times higher than the concentrations in the deeper layers after a heavy rain event. However, in the rainy summer of 2012, we could not link the rain events with the C_{CH_4} concentrations, probably because the water column stratification was weak, enabling efficient mixing, and thus any CH_4 inputs from the shoreline areas were efficiently diluted. Similarly, the temperature stratification in Valkea-Kotinen was broken as the result of a heavy rain and wind event and the input of CO_2 -rich water from the riparian zone became diluted (Rasilo *et al.* 2012). Since the bottom water of Kuivajärvi remained oxic throughout the winter and very little excess CH_4 was built up under the ice and high gas concentrations after ice melt were found only in the surface water, our results also strongly suggest that the spring peak in flux values was due to lateral transport. Unfortunately, the study by Dinsmore *et al.* (2013) on stream discharge and gases in the inlet of Kuivajärvi dealt solely with CO_2 and thus could not lend support to our CH_4 results.

The effects of weather patterns and water column stability were most clear in emissions

of N_2O , which were significantly higher in 2012 when summer stratification was weak. In 2012, NO_3^- -N concentrations, a substrate for denitrification, were also higher than in 2011, probably due to heavy rains and leaching from the catchment. A positive correlation between N_2O and NO_3^- -N indicates that substrate availability is crucial for denitrification and N_2O production, as shown previously by Rissanen *et al.* (2013). The low levels of NO_3^- in lakes in Finland thus explain the inefficiency and low rates of denitrification (Rissanen *et al.* 2013), and also the low N_2O emissions. The sampling in our study was not specifically designed for studies on processes producing N_2O , while focusing the sampling on oxic/anoxic boundary layers would probably give better insight into coupling the DOM decomposition (CO_2 production) and N_2O production processes. In autumn 2012, the slightly elevated N_2O emissions very likely originated from water masses close to the bottom, because the concentrations of N_2O throughout the water column increased approx. one week after the high concentrations were first measured deeper in the water column. At the same time, the water column stability was very low and thus mixing was efficient. However, in autumn 2011 the high N_2O concentrations near the sediment disappeared at a depth of 7 m and did not increase the emissions at the surface, probably due to more gradual break-up of the temperature stratification that year. In general, the N_2O concentrations were higher in Kuivajärvi than previously recorded in Finnish lakes (Huttunen *et al.* 2004), but comparable to those in lakes in Switzerland (Mengis *et al.* 1997). However, the concentrations as well as fluxes of both N_2O and CH_4 were negligible compared with those of CO_2 , as also found by Huttunen *et al.* (2003, 2004) in lakes in Finland with size and nutrient levels similar to those of Kuivajärvi. Although N_2O has 298 times higher GWP than CO_2 , in 2012 the annual GWP of CO_2 emission from Kuivajärvi was over 30 times higher than that of N_2O . The GWP of annual CO_2 emissions also exceeded that of CH_4 by approximately 20-fold, even though in productive urban lakes suffering from hypolimnetic anoxia, the GWP of CH_4 can be as much as 33% of the lake's annual total GWP (López Bellido *et al.* 2011, 2012a).

In conclusion, weekly measurements of CO₂, CH₄ and N₂O and calculated annual emissions of these gases revealed that boreal Kuivajärvi was a constant source of CO₂ and CH₄ throughout the ice-free period, but a source of N₂O only when the water column stability in summer was low. The emissions of all the gases studied peaked right after ice-out, but the concentration profiles showed significant build-up under the ice only for CO₂ during winter, and therefore, in spring at least the high peak of CH₄ most likely originated mainly from the catchment. The springtime emission of CO₂ lasted longer and contributed more to the total annual emission than reported previously for boreal lakes, also suggesting the presence of some external sources of CO₂. Hypolimnetic hypoxia in summer resulted in maximum concentrations of CH₄ and N₂O near the bottom sediments, but only contributed to the elevated emissions of N₂O in autumn 2012; otherwise, high concentrations near the sediment did not affect the surface concentrations. The unstable water column in summer 2012 increased the CO₂ and N₂O emissions, but prevented hypoxia and thus decreased the CH₄ concentrations in the hypolimnion. Although production of these gases is strongly coupled through OM decomposition, we will need specifically designed sampling protocols focusing on oxic/anoxic boundary layers to reveal these combined processes in detail. From the global-warming perspective, the lacustrine emissions of CO₂ were by far the most significant and the CH₄ and N₂O emissions were negligible in this very typical boreal lake.

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